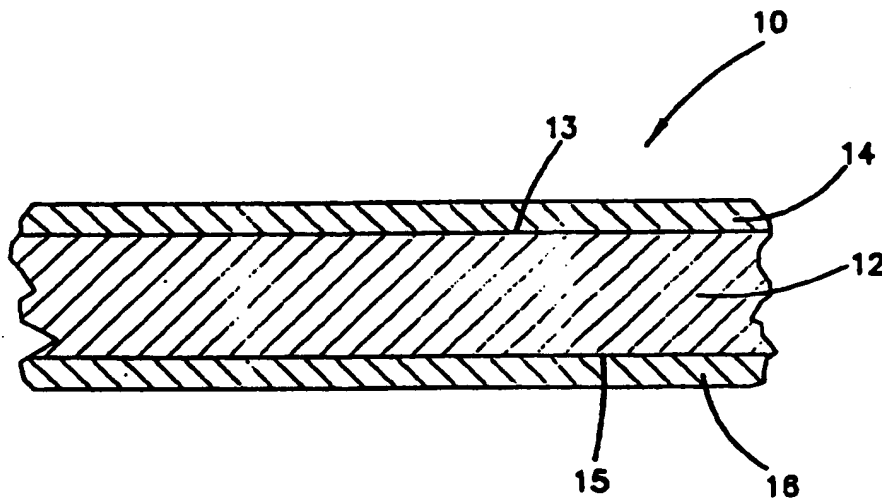




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B32B 27/08, 27/10, 27/36, C08G 59/02, 63/02, 63/06, 63/08, 63/12, 63/16, 65/02</b>		<b>A1</b>	(11) International Publication Number: <b>WO 97/11845</b> (43) International Publication Date: <b>3 April 1997 (03.04.97)</b>
(21) International Application Number: <b>PCT/US96/15682</b> (22) International Filing Date: <b>30 September 1996 (30.09.96)</b>  (30) Priority Data: 08/535,706      28 September 1995 (28.09.95)      US 08/642,329      3 May 1996 (03.05.96)      US  (71) Applicant: <b>CARGILL, INCORPORATED [US/US]; 15407 McGinty Road West, Minneapolis, MN 55440 (US).</b>  (72) Inventors: <b>EL-AFANDI, Ali, Zakareya; 2150 Parkview Lane, Woodbury, MN 55125 (US). GRUBER, Patrick, Richard; 10951 Flanders Court NE, Blaine, MN 55449 (US). KOLSTAD, Jeffrey, John; 16122 Ringer Road, Wayzata, MN 55391 (US). LUNT, James; 16008 Adeline Lane, Minnetonka, MN 55391 (US). RYAN, Christopher, M.; 16251 - 125th Avenue North, Dayton, MN 55327 (US). NANGERONI, James, Francis; 16 Charter Circle, Doylestown, PA 18901 (US). BUEHLER, Nancy, Uzelac; 15163 Bluebird Street, Andover, MN 55304 (US). HART-MANN, Mark; 5474 Sanibel Drive, Minnetonka, MN 55343 (US). RANDALL, Jed, Richard; 3026 - 39th Avenue S., Minneapolis, MN 55406 (US). BROSCHE, Andrea, Lee; 6470 Undestad Street, Eden Prairie, MN 55346 (US).</b>		(74) Agent: <b>BRUESS, Steven, C.; Merchant, Gould, Smith, Edell, Welter &amp; Schmidt, P.A., 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402-4131 (US).</b>  (81) Designated States: <b>AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b>	
		Published With international search report.	

(54) Title: COMPOSTABLE MULTILAYER STRUCTURES AND ARTICLES PREPARED THEREFROM



## (57) Abstract

A compostable multilayer structure is provided by the present invention. The multilayer structure can be in the form of a film, sheet, laminate, and the like, and includes a core layer (12) having a first surface (13) and a second surface (15), a first blocking reducing layer (14) covering the first surface of the core layer, and a second blocking reducing layer (16) covering the second surface of the core layer. The core layer includes a polymer composition of a hydrolyzable polymer containing a lactic acid residue and has a glass transition temperature (T<sub>g</sub>) below about 20 deg. C. The first and second blocking reducing layers include a polymer composition of a hydrolyzable polymer and have a T<sub>g</sub> above about 50 deg. C. The multilayer structure can be used for preparing bags and wrappers.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**COMPOSTABLE MULTILAYER STRUCTURES  
AND ARTICLES PREPARED THEREFROM**

**Field of the Invention**

The present invention relates to compostable  
5 multilayer structures and articles prepared from  
compostable multilayer structures.

**Background of the Invention**

Plastic trash bags and wrappers are primarily  
10 made of hydrocarbon polymers such as polyethylene,  
polypropylene, or polyvinyl polymers. While hydrocarbon  
polymers can be useful for commercially manufacturing  
trash bags and wrappers having adequate flexibility and  
puncture and tear resistance, they are resistant to  
15 degradation and mineralization and have a tendency to  
build up in land fills. Under most conditions,  
hydrocarbon polymers take a long time to decompose. In  
addition, hydrocarbon polymers are not manufactured from  
renewable resources.

20 Attempts have been made at developing  
thermoplastic films having degradable properties. For  
example, U.S. Patent No. 4,133,784 describes degradable  
mulch films with improved moisture resistance prepared  
from starch and ethylene/acrylic acid copolymers. U.S.  
25 Patent No. 5,091,262 describes a multilayer polyethylene  
film containing a starch filled inner layer, and  
prodegradant filled outer layers. U.S. Patent No.  
5,108,807 describes a multilayer thermoplastic film  
having a core layer made of polyvinyl alcohol, and outer  
30 layers made of polyethylene and prodegradant. U.S.  
Patent No. 5,391,423 describes multilayer films prepared  
from various biodegradable polymers for use in  
disposable absorbent products, such as diapers,  
incontinent pads, sanitary napkins, and pantyliners.

35 Many biodegradable polymers have been found to  
possess the desirable characteristics of  
biodegradability and compostability. At room

temperature, however, many biodegradable polymers are either too brittle to provide the desired puncture and tear resistance necessary for commercially acceptable trash bags, or they do not have adequate stability for storage and transport. In addition, many biodegradable polymers are difficult to process into films using commercial manufacturing lines.

### Summary of the Invention

Compostable multilayer structures with desired properties of flexibility and tear resistance are provided by the present invention. The compostable multilayer structures are preferably in the form of films, sheets, laminates and the like. The compostable multilayer structures can be manufactured into disposable consumer products such as bags, wrappers, cups, and the like, which can degrade when subjected to composting conditions. Preferably, the multilayer structure is in the form of a film.

The compostable multilayer structures can be provided in various layered arrangements. A preferred compostable multilayer structure includes a core layer having a first surface and a second surface, a first blocking reducing layer covering the first surface of the core layer, and a second blocking reducing layer covering the second surface of the core layer. Preferably, the core layer has a glass transition temperature ( $T_g$ ) below about 20°C, and at least one of the first and second blocking reducing layers includes a semicrystalline polymer composition and/or has a glass transition temperature above about 50°C.

Applicants discovered that certain desirable properties of compostable polymer compositions, such as flexibility, tear resistance, and puncture resistance, can be adjusted by controlling the glass transition temperature thereof. For example, for many compostable polymer compositions, such as hydrolyzable polymer compositions, reducing the ( $T_g$ ) provides a layer having

increased flexibility, tear resistance, and puncture resistance to commercially acceptable levels for bags and wrappers. In addition, Applicants discovered that certain polymers compositions can be used to provide blocking reducing layers when applied over the compostable polymer compositions having increased flexibility, tear resistance, and puncture resistance. As used in the context of the present invention, blocking occurs when polymer composition layers fuse or stick together. The extent of blocking is evaluated relative to the degree of fusion between the layers or tackiness of the layers. Many polymer compositions having low glass transition temperature have been found to possess increased incidence of blocking. Applicants discovered, however, that resistance to blocking can be adjusted by controlling the glass transition temperatures. For many compostable polymer compositions, such as certain hydrolyzable polymer compositions, an increased glass transition temperature tends to reduce blocking. In addition, Applicants additionally discovered that controlling the crystallinity of a polymer composition can provide reduced blocking.

The layers of the compostable multilayer structures are preferably made of materials which are compostable, such as polymer compositions which include, for example, hydrolyzable polymers.

The polymers which can be used to provide the layers of the multilayer structure should have a number average molecular weight in the range of about 50,000 to about 200,000, and a weight average molecular weight in the range of about 100,000 to about 600,000. To provide sufficient flexibility and puncture and tear resistance, it has been found that the polymer used to prepare the core layer should have a number average molecular weight between about 80,000 and 200,000, more preferably between about 90,000 and 175,000, and even more preferably between about 100,000 and 150,000. The

blocking reducing layers should have a number average molecular weight above about 50,000.

It is understood that the low glass transition temperature is responsible for providing the multilayer structure with desired flexibility and tear resistance. Accordingly, it is desirable to provide the glass transition temperature of the core layer below the temperatures at which the multilayer structure will be used. It has been found that for most conditions of use at room temperature, a  $T_g$  below about 20°C should be acceptable. At cooler conditions, it is preferred that the core layer should have a  $T_g$  below about 5°C, and under more extreme conditions, a  $T_g$  below about -10°C would be preferred.

A preferred technique for reducing the glass transition temperature of the core layer is to incorporate therein an effective amount of plasticizers into the polymer composition which forms the core layer. Generally, this means that the plasticizer can be included to provide a concentration level of about 10 to 35 percent by weight, and more preferably a concentration level of about 12 to 30 percent by weight. It is preferred that the plasticizer is biodegradable, non-toxic, compatible with the resin, and relatively nonvolatile.

When the core layer has a glass transition temperature below the temperature of use of the multilayer structure, it has been found that the core layer suffers from blocking. It should be appreciated that blocking occurs when polymer layers fuse together. The extent of blocking is a function of the degree that the layers fuse together. Layers which are highly blocked will be almost totally fused together. Blocking is a particularly undesirable property for certain articles such as bags and wrappers which are commonly stored in a roll or other arrangement where the layers are in contact.

Applicants have found that blocking can be reduced by the incorporation of blocking reducing layers in the compostable multilayer structure.

In an alternative embodiment of the present invention, the compostable multilayer structure can be provided as a two layer structure having a core layer and a blocking reducing layer. It is believed that this compostable multilayer structure can be stored in the form of a roll so that both sides of the core layer are adjacent a blocking reducing layer.

Compostable multilayer sheets are provided by the present invention. The sheet has a thickness greater than 10 mils (0.010 inch). The sheet can be used as thermoformed rigid container, cups, tubs, dinnerware, etc. In most applications, it is understood that the sheet will have a thickness less than 150 mils.

A compostable film is provided by the present invention, wherein the compostable film includes a lactic acid residue containing polymer, and has a tear resistance of greater than 50 gm<sub>f</sub>/mil at 23°C according to ASTM D1922-89, and exhibiting substantially no blocking when folded bck on itself and held together under pressure of 180 g/in<sup>2</sup> at 50°C for two hours, and preferably for 24 hours. Preferably, the film has a tear resistance of at least 65 gm<sub>f</sub>/mil, and more preferably at least 80 gm<sub>f</sub>/mil at 23°C according to ASTM D1922-89.

#### Brief Description of the Drawings

FIGURE 1 is a cross-sectional view of a multilayer structure in the form of a film according to the principles of the present invention;

FIGURE 2 is a cross-sectional view of an alternative embodiment of a multilayer structure in the form of a laminate having a paper substrate according to the principles of the present invention; and

FIGURE 3 is a graph comparing the rate of biodegradation of the multilayer film of Example 2, kraft paper, and cellulose.

5                    Detailed Description of the Invention

          The present invention relates to a multilayer structure having compostable properties. This means that the multilayer structure will break down and become part of a compost upon being subjected to physical,  
10    chemical, thermal, and/or biological degradation in a solid waste composting or biogasification facility. As used in this application, a composting or biogasification facility has a specific environment which induces rapid or accelerated degradation.  
15    Generally, conditions which provide rapid or accelerated degradation, compared with storage or use conditions, are referred to herein as composting conditions. In the context of the present invention, the multilayer structure may be referred to as a compostable multilayer  
20    structure.

          In order to provide a compostable multilayer structure, the components of the multilayer structure should be compostable and biodegradable during composting/biogasification, or in compost amended soil,  
25    at a rate and/or extent comparable to that of known reference materials such as cellulose or paper. Basically, this means that the components should be degradable within a time frame in which products made therefrom, after use, can be recycled by composting and  
30    used as compost. It should be understood that certain materials such as hydrocarbons and other polymeric resins including polyethylenes, polypropylenes, polyvinyls, polystyrenes, polyvinyl chloride resins, urea formaldehyde resins, polyethylene terephthalate  
35    resins, polybutylene terephthalate resins, and the like are not considered compostable or biodegradable for purposes of this invention because they take too long to degrade when left alone in a composting environment.



The rate and extent of biodegradation of the multilayer structure can be correlated to known biodegradable materials, such as kraft paper or cellulose, using ASTM D5338-92 Test Method for

5 Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions. This is a laboratory test which compares the rate of biodegradation of a test sample to that of a known biodegradable material by determining the amount of CO<sub>2</sub>

10 evolved from the compost with and without the test sample. A modified version of the ASTM D5338-92 test can be used to more conveniently approximate large scale composting conditions. This modified test is referred to as the first modified test and is performed according

15 to ASTM D5338-92 except that a constant temperature of 58°C is provided. The amount of material biodegraded is calculated based upon measuring the amount of carbon dioxide evolved therefrom. A second modified version of ASTM D5338-92 can be used to determine the degradation

20 at soil conditions. The second modified test is carried out according to ASTM D5338-92 except that a temperature of 30°C is used and the media is soil at approximately 70% of its moisture holding content (ASTM D 425).

Test results for biodegradation according to

25 the first modified ASTM D5338-92 test are provided in FIG. 3 where the cumulative percent biodegradation (referred to as the biodegradation value) is measured as a function of time for the multilayer structure prepared in Example 2, kraft paper, and cellulose. The details

30 of this test are described in Example 9. For the results plotted in FIG. 3, a biodegradation value of 70 percent at 40 days means that at least 70 percent of the carbon in the multilayer structure has been converted to carbon dioxide and microbial biomass after composting

35 under conditions of the first modified test for 40 days. For most multilayer structures of the present invention, it is preferred that they have a biodegradation value of at least 50 percent after 40 days, and even more

preferably at least 60 percent after 40 days. In addition, it is preferred that they possess a biodegradation value of at least about 70 percent after 60 days. For slower materials, biodegradation values of  
5 at least about 20 percent after 40 days and/or at least about 30 percent after 60 days can be provided.

Another way of characterizing the rate and extent of biodegradation of the multilayer structure of the invention is to compare it with the rate and extent  
10 of biodegradation of known compostable and biodegradable materials such as kraft paper and cellulose. Generally, it is desirable that the multilayer structure will have a biodegradation value which is at least about 50 percent, and more preferably at least about 60 percent,  
15 of the biodegradation value of kraft paper or cellulose after 40 days in a standard compost as provided in ASTM D5338-92.

It should be understood that the multilayer structure of the invention can include materials which  
20 are not compostable or biodegradable under short period composting conditions.

The multilayer structure of the invention can be provided as films, sheets, laminates, and the like. Films can be used in applications such as disposable  
25 bags, wrappers, personal hygiene products, packaging materials, agricultural mulch films, and the like. Exemplary disposable bags include trash bags, sandwich or snack bags, grocery bags, waste bin liners, compost bags, food packaging bags and the like. Exemplary  
30 disposable wrappers include food wrappers such as fast food wrappers, food packaging films, blister pack wrappers, skin packaging and the like. Sheets can be used in applications including thermoformed rigid containers, cups, tubes, dinnerware, cup lids, deli  
35 trays and the like. Laminates include coated paper which can be used, for example, as boxes, multiwall bags, multiwall containers, spiral wound tubes (e.g., mailing tubes), and the like. In situations where the

multilayer structure is in the form of a film or sheet, it may be desirable to ensure that the film or sheet possess the properties of tear resistance, quietness, and impact resistance. Transparent structures may also be of benefit for any packaging application, where it is desirable to see the package contents. The multilayer structure of the invention can also be prepared using coextrusion blow molding, to directly produce articles such as rigid containers, tube, bottles, and the like. For certain applications, such as, use in a compostable lawn refuse bag, it may be desirable to have the multilayer structure substantially transparent to visible light. This allows rapid determination of the contents before shipping to a compost facility, or identification of contents under a wrapper.

Applicants found that presently available biodegradable polymers do not generally possess desirable physical properties for use as single layer films or sheets because they have high glass transition temperatures, poor tear resistance structures which do not rapidly crystallize (if it has a low Tg), low melting point, or are difficult to process on conventional machines. These particular problems are often encountered when trying to process biodegradable polymers in conventional process equipment.

It is understood that crystallinity is an important characteristic of a polymer and can be relied upon to reduce blocking. As discussed above, blocking occurs when films or other structures fuse together. It is a particularly undesirable property when it is exhibited by trash bags because it causes the sides of the bag to stick together, thereby preventing the bag from opening. It is believed that blocking is a function of the rate and extent of crystallization of a polymer. For example, it is understood that if the polymer crystallizes sufficiently quickly, it is believed that the tendency to block can be reduced. On the other hand, polymers which crystallize slowly will

have a tendency to block in the process equipment when recently formed films or sheets are brought together causing them to fuse. An example of a polymer which does not crystallize sufficiently quickly under  
5 processing conditions is poly(caprolactone). It is believed, however, that for many polymers such as poly(caprolactone), processing conditions can be modified to reduce blocking. For example, it is believed that the double bubble blown film process can  
10 reduce blocking in poly(caprolactone) polymer compositions.

Some biodegradable polymers are not suitable for single layer bags because they have a melting point ( $T_m$ ) which is too low. A low  $T_m$  renders a polymer  
15 difficult to process, and requires cooling below its  $T_m$  to induce crystallization. Several aliphatic polyesters have a  $T_m$  which is too low. Also, if the storage or use temperature exceeds  $T_m$  then the film will tend to fuse and lose integrity. An exemplary aliphatic polyester,  
20 such as polycaprolactone, requires a crystallization temperatures of room temperature or below which is difficult to achieve in most blown film or cast film facilities. Exemplary aliphatic polyesters having desirable  $T_m$ , but  $T_g$  which is too high, include  
25 polyglycolide, polylactide, and poly(hydroxy butyrate).

Applicants have found ways to provide biodegradable polymer compositions having glass transition temperatures lower than ambient temperature. Various methods within the scope of the invention  
30 include providing blends of polymers or other additives, using copolymers, incorporating a plasticizer, and the like. These methods are discussed in more detail below. The resulting biodegradable polymer compositions have a glass transition temperature lower than ambient  
35 temperature. It has been observed that they can suffer from blocking when formed into a film or sheet. In order to overcome the blocking problem, Applicants discovered that certain biodegradable polymer

compositions, such as, amorphous polymer compositions having a high  $T_g$  or semi-crystalline polymer compositions, can be formed into thin layers and used as blocking reducing layers.

5

#### **The Compostable Multilayer Structure**

Now referring to FIG. 1, a preferred embodiment of the multilayer structure according to the present invention is shown at reference numeral 10 in the form of a film. The multilayer film 10 includes a core layer 12, a first blocking reducing layer 14, and a second blocking reducing layer 16. The first blocking reducing layer 14 covers the first surface 13 of the core layer 12, and the second blocking reducing layer 16 covers the second surface 15 of the core layer 12. In the arrangement shown in FIG. 1, the core layer 12 is in contact with both the first blocking reducing layer 14 and the second blocking reducing layer 16. It should be understood, however, that for one layer to "cover" another layer, it is not necessary that the layers be in contact with each other. It should be appreciated that another layer or material can be placed therebetween. For example, a layer of adhesive, polymer, foil, or other material, such as paper, can be placed between the core layer and the blocking reducing layer. Various properties, such as, vapor resistance, chemical resistance, adhesion, tensile strength, and the like, can be provided by selecting layers in addition to those shown in the multilayer film 10.

30

It should be appreciated that the multilayer film can be provided without a second blocking reducing layer. The film could be stored in roll form so that the core layer contacts both sides of the blocking reducing layer. The film could then be unrolled prior to use, for example, as a wrapper or covering.

35

In an alternative embodiment of the invention shown in FIG. 2, a laminated paper product 20 is provided. The laminated paper product has a paper

substrate 21, a core layer 22, and a blocking reducing layer 24 covering the core layer 22. It should be appreciated in this embodiment that the paper substrate 21 can also function as a blocking reducing layer.

5 It is generally desirable for the blocking reducing layers to be as thin as possible to provide sufficient resistance to blocking and sufficient coverage over the core layer. In most structures, including films, sheets and laminates it is believed  
10 that the blocking reducing layers will be considered films, and may herein be referred to as films in the context of the present invention. It is understood that the core layer, generally, is primarily responsible for providing flexibility and tear and puncture resistance.  
15 Accordingly, it is usually preferred to maximize the core layer relative to the blocking reducing layers.

For many applications where the blocking reducing layer is extruded, the thickness of the blocking reducing layer should be sufficient to provide  
20 a continuous layer and/or desired blocking resistance. It is believed that this usually corresponds with a lower limit of at least about 0.05 mil. If the thickness of the blocking reducing layer is much less than 0.05 mil, it has been found to be difficult to  
25 maintain a continuous coating. In most applications, it is believed that the thickness of the blocking reducing layers should be less than 0.5 mil, more preferably less than 0.3 mil, and even more preferably less than 0.1 mil. The core layer can be essentially any size so long  
30 as it provides the desired properties.

For most multilayer films, such as the one depicted in FIG. 1, it is believed that the total thickness of the film will usually be less than about 10 mil, and more preferably between about 1 mil and about 3  
35 mils. Since it is desirable to keep the ratio of thicknesses of a blocking reducing layer to the overall thickness of the film as low as possible, the percentage of the blocking reducing layer to the overall thickness

should be between about 5% and 25%. The percentage of the combined thickness of the blocking reducing layers to the overall thickness of the multilayer structure should be less than about 40%, and more preferably less than about 30%. Accordingly, at least about 60% of the thickness of the multilayer structure should be core layer, more preferably at least 70%.

It is believed that a multilayer sheet will have a thickness of at least about 10 mil or greater. Multilayer layer structures which include a paper layer or substrate can have a thickness, exclusive of paper substrate, of 0.5-3 mil. Generally, the thickness of the blocking reducing layers will have essentially the same values described above so long as they provide sufficient blocking resistance.

Exemplary types of hydrolyzable polymers include poly(trimethylene carbonate) and polyesters such as poly(lactide), poly(lactic acid), poly(glycolide), poly(hydroxy butyrate), poly(hydroxy butyrate-co-hydroxy valerate), poly(caprolactone), poly(1,5-dioxepan 2-one), poly(1,4-dioxepan 2-one), poly(p-dioxanone), poly(delta-valerolactone), and other polyesters such as those containing residues of C<sub>2</sub>-C<sub>10</sub> diols, and terephthalic acid, and the like. The polymers can be copolymers and polymer blends of the above polymers. Preferred polyesters are generally aliphatic polyesters which hydrolyze to biodegradable units.

Lactic acid residue containing polymers are particularly preferred for use in the present invention due to their hydrolyzable and biodegradable nature. One theory of the degradation of lactic acid residue containing polymers is that they can be degraded by hydrolysis at hydrolyzable groups to lactic acid molecules which are subject to enzymatic decomposition by a wide variety of microorganisms. It should be appreciated, however, that the precise mechanism of degradation is not a critical feature of the present invention. Rather, it is sufficient that one recognizes

that polymers which provide similarly rapid degradation to naturally occurring end products can be useful in the present invention. U.S. Patent No. 5,142,023 discloses, generally, a continuous process for the manufacture of lactide polymers from lactic acid. Related processes for generating purified lactide and creating polymers therefrom are disclosed in U.S. Patent Nos. 5,247,058; 5,247,059; and 5,274,073. It should be appreciated that selected polymers from these patents having the physical properties suitable for use in the present invention can be utilized. Generally, polymers according to U.S. Patent No. 5,338,822 and U.S. Patent Application Serial No. 08/279,732 can be used in the present invention. Exemplary lactic acid residue containing polymers which can be used are described in U.S. Patent Nos. 5,142,023; 5,274,059; 5,274,073; 5,258,488; 5,357,035; 5,338,822; and 5,359,026, and U.S. Patent Application Serial Nos. 08/110,424; 08/110,394; and 08/279,732. Polylactide polymers which can be used in the invention are available under the tradename EcoPLA®.

By now it should be appreciated that the term lactic acid residue containing polymer includes polymers containing about 50%, by weight, or more lactic acid residue units which, under certain conditions, will hydrolyze to lactic acid or derivative thereof. The remaining components of the lactic acid residue containing polymers can include non-lactic acid residues. Preferably, the lactic acid residue containing polymer is least about 70%, and more preferably at least about 90%, lactic acid residue. In a preferred embodiment, the lactic acid residue containing polymer contains less than about 2%, by weight, non-lactic acid residue.

Lactic acid residue containing polymers are generally prepared from monomers which include lactic acid, lactide, or combination thereof. It should be understood that other structural units which, when polymerized, have a structure similar to polymerized



lactic acid or lactide can be used. Rather than focusing on how the lactic acid residue containing polymers are prepared, it should be understood that what is important is that the lactic acid residue containing polymers have characteristics which render them susceptible to hydrolysis and thereby enhance degradability or biodegradability. It is these characteristics which are important rather than the strict chemical composition of the polymer. However, polymers which are considered lactic acid residue containing polymers include poly(lactide) polymers, poly(lactic acid) polymers, and copolymers such as random and/or block copolymers of lactide and/or lactic acid. Lactic acid components which can be used to form the lactic acid residue containing polymers include L-lactic acid and D-lactic acid. Lactide components which can be used to form the lactic acid residue containing polymers include L-lactide, D-lactide, and meso-lactide.

A particularly preferred type of polylactide polymer includes viscosity modified polylactide which is described in detail in U.S. Patent No. 5,359,026 and WO 95/04097. Viscosity modified polylactide polymers are important because they provide desirable processing characteristics such as reduced viscosity, increased melt strength, and hence improved bubble stability.

Particularly preferred viscosity modified polylactide polymers include copolymers of lactide and epoxidized multifunctional oil such as epoxidized linseed oil and epoxidized soybean oil. In many situations, it is preferred that the polymer is prepared from 0.1 to 0.5 weight percent epoxidized multifunctional oil and molten lactide monomer. Catalyst can be added, and the mixture can be polymerized between about 160°C and 200°C. The resulting polymer preferably has a number average molecular weight of about 80,000 to about 140,000.

As discussed above, many biodegradable polymers such as non-plasticized polylactic acid

polymers are generally too brittle for use as single layer flexible films and/or sheets. Their  $T_g$  is generally above 50°C, and it has been observed that they provide a film or sheet having low impact resistance and tear resistance. Tear resistance of a typical polylactide film having a  $T_g$  above 50°C is less than about 6 gm<sub>f</sub>/mil. Other biodegradable polymers, including certain aliphatic polyesters, exhibit poor tear strength. These physical properties render films or sheets prepared therefrom poor candidates for use as bags or wrappers. Articles such as trash bags, grocery bags, food wrappings, and the like should be flexible and resistant to tearing and puncturing.

Applicants discovered that by lowering the glass transition temperature ( $T_g$ ) of biodegradable polymers to about 20°C or less, it is possible to provide a film or sheet having improved flexibility and tear and puncture resistance. More preferably, it is desirable to lower the  $T_g$  to below about 5°C, and more preferably below about minus 10°C. These glass transition temperature should be below the temperature at which the polymer is used. When the biodegradable polymer is a lactic acid residue containing polymer, a preferred method for lowering the glass transition temperature ( $T_g$ ) is by adding plasticizer thereto. As demonstrated in Example 1, plasticizer can be added to a polylactide polymer to lower the glass transition temperature ( $T_g$ ) from 60°C, without plasticizer, to 19°C at a level of 20 percent, by weight, plasticizer.

The selection of the plasticizer can involve consideration of several criteria. Since it is generally desirable to provide as much biodegradability as possible, it is preferred to use a plasticizer which is biodegradable, non-toxic, compatible with the resin, and relatively nonvolatile. Plasticizer in the general classes of alkyl or aliphatic esters, ether, and multifunctional esters and/or ethers are preferred. These include alkyl phosphate esters, dialkylether diesters,

tricarboxylic esters, epoxidized oils and esters, polyesters, polyglycol diesters, alkyl alkylether diesters, aliphatic diesters, alkylether monoesters, citrate esters, dicarboxylic esters, vegetable oils and their derivatives, and esters of glycerine. Preferred plasticizer are tricarboxylic esters, citrate esters, esters of glycerine and dicarboxylic esters. More preferably, citrate esters are preferred since it is believed that these esters are biodegradable. These plasticizer can be obtained under the names Citroflex A-4<sup>®</sup>, Citroflex A-2<sup>®</sup>, Citroflex C-2<sup>®</sup>, Citroflex C-4<sup>®</sup> (from Morflex).

It should be appreciated that plasticizer containing aromatic functionality or halogens are less preferred because of their possible negative impact on the environment. For example, appropriate non-toxic character is exhibited by triethyl citrate, acetyltriethyl citrate, tri-n-butyl citrate, acetyltri-n-butyl citrate, acetyltri-n-hexyl citrate, n-butyltri-n-hexyl citrate and acetyltriethyl citrate, tri-n-butyl citrate, diisobutyl adipate, diethylene glycol dibenzoate, and dipropylene glycol dibenzoate. Appropriate compatibility is exhibited by acetyltri-n-butyl citrate, acetyltriethyl citrate, tri-n-butyl citrate, diisobutyl adipate, diethylene glycol dibenzoate, and dipropylene glycol dibenzoate. Other compatible plasticizers include any plasticizer or combination of plasticizer which can be blended with lactic acid residue containing polymer and are either miscible therewith or which form a mechanically stable blend.

Volatility is determined by the vapor pressure of the plasticizer. An appropriate plasticizer should be sufficiently non-volatile such that the plasticizer stays substantially in the composition throughout the process needed to produce the multilayer structure, and to provide desired properties when the structure is used. Excessive volatility can lead to fouling of

process equipment, and can result in undesired plasticizer migration. Preferred plasticizer should have a vapor pressure of less than about 10 mm Hg at 170°C, and more preferred plasticizer should have a  
5 vapor pressure of less than 10 mm Hg at 200°C.

Internal plasticizer, which are bonded to the lactic acid residue containing polymer, may also be useful in the present invention. Exemplary plasticizer which can be bonded to the polymer include epoxides.

10 Applicants have found that while reducing the  $T_g$  of lactic acid residue containing polymers enhances flexibility and tear strength, it also increases or promotes blocking. This feature is demonstrated by the data in Table 1 in Example 1.

15 Applicants found that multilayer structures could be created which were relatively resistant to blocking over time and which retained the desirable properties of a plasticized lactic acid residue containing polymer composition, such as, elongation and  
20 tear resistance. The blocking was reduced by incorporating blocking reducing layers which cover the core layer of plasticized lactic acid residue containing polymer. The blocking reducing layers could have a variety of compositions, provided that they reduce  
25 blocking.

#### **The Blocking Reducing Layer**

Five preferred types of compositions for forming the blocking reducing layers are described  
30 below. A preferred first composition for preparing the blocking reducing layer includes amorphous lactic acid residue containing polymer having a  $T_g$  above 50°C. It is believed that the high glass transition temperature of the amorphous lactic acid residue containing polymer is  
35 responsible for reducing or preventing blocking. Thus, blocking can be reduced provided that the ambient or use temperature is below the  $T_g$  of the blocking reducing layer. It is believed that at temperatures below the  $T_g$ ,

of the polymer, the molecules in the polymer are not sufficiently mobile to cause blocking.

A preferred second composition which can be used for preparing the blocking reducing layer includes  
5 semicrystalline lactic acid residue containing polymer. A semicrystalline lactic acid residue containing polymer will generally have an optical purity of greater than 85% either R or S lactic acid residues, although the overall composition can be less optically pure if the  
10 polymer is a block copolymer, rather than random. The semicrystalline lactic acid residue containing polymer provides blocking resistance to higher temperatures than the amorphous lactic acid residue containing polymer, with no blocking observed even at temperature of 90°C.

15 A preferred third composition which can be used for preparing the blocking reducing layer includes lactic acid residue containing polymer and a high glass transition temperature polymeric additive for reducing blocking. Preferred high  $T_g$  polymeric additives include  
20 polymers with a  $T_g$  greater than about 50°C, and more preferably greater than about 90°C. The most preferred high  $T_g$  polymeric additives are biodegradable and derived from renewable resources. Exemplary preferred high  $T_g$  polymeric additives include cellulose acetate, cellulose  
25 propionate, cellulose butyrate, cellulose acetate propionate, cellulose acetate butyrate, cellulose propionate butyrate, terpene resins and rosin and rosin esters derived from tree sap.

A preferred fourth composition which can be  
30 used for preparing the blocking reducing layer includes a lactic acid residue containing polymer and a semicrystalline polymeric additive. Preferred semicrystalline polymeric additives will have a melting point above 90°C and more preferably above 120°C. The  
35 most preferred semicrystalline polymeric additives are biodegradable and derived from renewable resources. Preferred semicrystalline polymeric additives include aliphatic polyester with melting points above 90°C.

Exemplary preferred semicrystalline polymeric additives include poly(hydroxy butyrate), poly(hydroxy butyrate-co-hydroxy valerate), polybutylene(succinate), polybutylene(succinate-adipate copolymer),  
5 polyethylene(succinate), and polyethylene(succinate-adipate copolymer). It is believed that poly(glycolide), poly(lactide), or the stereocomplex of poly(L-lactide) and poly(D-lactide) might also be suitable for use as antiblocking agents.

10 It is understood that the semicrystalline polymeric additives should be present in an amount of between about 5-70% by weight of blocking reducing layer, more preferably between about 10 and 50% by weight. In the case of additive such as  
15 polyhydroxybutyrate (PHB) polymers and polyhydroxy butyrate/valerate copolymers (PHBV), it is preferred that they be present in an amount of about 10% by weight of blocking reducing layer.

Without being bound by theory, it is believed  
20 that the limited compatibility of the anti-blocking agent in the blocking reducing layer may be partly responsible for enhancing the anti-blocking characteristics thereof.

A preferred fifth composition which can be  
25 used for preparing the blocking reducing layer includes a rapidly crystallizable polymer having a high melting temperature ( $T_m$ ). Preferably, it also exhibits a low glass transition temperature ( $T_g$ ). It is believed that the rapid crystallization will facilitate processing by  
30 reudcing or preventing sticking and blocking film handling.

Polymer compositions having a low  $T_g$  and high  $T_m$  are desirable because they can provide rapid crystallization after processing. Typically, in order  
35 for a polymer composition to exhibit rapid crystallization, it needs to be well below its  $T_m$ . Under normal processing condition, the polymer composition should therefore have a  $T_m$  above about 80°C and below

about 200°C, and preferably below about 170°C. A  $T_m$  of 80°C is believed to be high enough so that a polymer can crystallize during typical blown film production. A  $T_m$  of 80°C or higher will also provide excellent blocking performance under typical use and storage conditions. The upper limit on the  $T_m$  is determined by providing a composition which can be readily processable in line with a biodegradable polymer such as a lactic acid based polymer. Polymer compositions having a  $T_m$  above 200°C generally require processing conditions which make it difficult to provide on the same line as, for example, a plasticized polylactide polymer, even with the use of a multilayer die with distinct heating sections.

The glass transition temperature of the polymer composition should be relatively low in order to provide desired performance under certain applications. For example, a low glass transition temperature is particularly important for use in outdoor applications, such as lawn and leaf disposal bags. It has been observed that a low  $T_g$  in the outer layer can help to strengthen the bag properties which otherwise are born entirely by the core layer. In most applications, the  $T_g$  should be below about 10°C., and preferably below 0°C, and more preferably below -10°C.

The extent of crystallinity should be sufficient to provide an outer layer having a crystallinity of at least about 10 J/g based on the weight of the outer layer only, or roughly 3 J/g based on the weight of the film having a layered cross-section of 15/70/15 by weight of each layer. This is believed to be sufficient to give excellent blocking resistance. Preferably, the crystallinity of the outer layer can be greater than 30 J/g. In most applications, the crystallinity of the outer layer will be less than 100 J/g.

The preferred polymers to meet these criteria are generally based on aliphatic polyesters, produced either from ring opening reactions or from the

condensation of acids and alcohols. Typically, diols and diacids are reacted to form an aliphatic polyester by condensation polymerization. Often this limits the potential molecular weight to a number average molecular weight of less than 30,000, although, in some case, it may be as high as 50,000. To achieve higher molecular weights is generally very difficult. This molecular weight limit tends to result in polymers with poor tear strength, which is a critical property for film bag applications. Thus, these polymers, on their own, may have insufficient tear strength for a commercially acceptable film bag.

Aliphatic polyesters based on diacids and diols are available commercially and are generally preferred. The aliphatic polyesters with an even number of carbons in the diacid generally have a more crystalline nature than those with an odd number of carbons. The preferred aliphatic polyesters comprise the reaction products of a C<sub>2</sub>-C<sub>10</sub> diol with oxalic acid, succinic acid, adipic acid, suberic acid, sebacic acid, or mixtures and copolymers thereof. More preferred polyesters include polyethylene(oxalate), polyethylene(succinate), polybutylene(oxalate), polybutylene(succinate), polypentamethyl(succinate), polyhexamethyl(succinate), polyheptamethyl(succinate), or polyoctamethyl(succinate), mixtures or copolymers thereof, or copolymers of these with adipic acid. Especially preferred are polyethylene(succinate), polyethylene(succinate-co-adipate), polytubylene(oxylate), polybutylene(succinate), polybutylene(succinate-co-adipate), polybutylene(oxylate-co-succinate and/or adipate), and mixtures thereof. The polybutylene terminology in this case refers to the condensation product of 1,4 butane diol and polyethylene terminology refers to the condensation product of 1,2 ethan diol, also know as ethylene glycol. To ensure reasonable rates of crystallization and sufficiently high T<sub>m</sub>, it is



anticipated that any copolymers will contain at least 70 mole % of the primary diacid (on a diacid basis). The aliphatic polyesters may also contain units derived from non-aliphatic diacids, or esters, such as terephthalic acid or methyl terephthalate. The condensation products of diacids with polyether diols may also be useful as outer layers in the multilayer film application.

An exemplary preferred polymer is a polybutylene succinate homopolymer sold under tradename Bionelle 1000<sup>TM</sup> and is available from Showa Highpolymer Co., Ltd. It is believed that polybutylene(succinate-terephthalate copolymer) and polybutylene(adipate-terephthalate copolymer) will be useful in forming the blocking reducing layer.

15

#### Core Layer

In a preferred composition, the core layer will have a  $T_g$  below 20°C and more preferably below 10°C. In the case of a polymer composition including a lactic acid residue containing polymer, reduced  $T_g$  can be provided by a plasticizer level of about of 20 wt-% or more.

The core layer of the multilayer structure should be sufficiently flexible to be rolled or folded for packaging, to be useful for purpose intended. Preferably, the first layer should have sufficient flexibility to allow it to be folded over onto itself without cracking at the crease. It is preferred that a multilayer film according to the present invention would have a tensile modulus of less than 75,000 psi at 23°C when tested according to ASTM D-882 method A-3.

Pigments or color agents may also be added as necessary. Examples include titanium dioxide, clays, calcium carbonate, talc, mica, silica, silicates, iron oxides and hydroxides, carbon black and magnesium oxide.

Applicants have found that the presence of residual catalysts in the lactic acid residue containing polymer structure significantly affects the stability

thereof during processing. Accordingly, the catalyst level can be controlled as described in U.S. Patent No. 5,338,822.

5

### Examples

#### Example 1

#### Example Showing Inverse Relationship Between Tear Resistance and Blocking Resistance and Direct Relationship Between Plasticizer Level and $T_g$

A Leistritz 34 mm twin screw extruder was used to compound a mixture of components described below. The extrudate was cooled in a water bath and chopped into pellets. The pellets were then coated with 0.1% Ultra-Talc 609 to prevent agglomeration, dried at 30°C, and extruded through a flat die to form a structure for property testing.

The twin screw extruder was operated with zone 1 (pellet feed zone) at 150°C, zone 2 at 160°C, zones 3-6 at 170°C, zones 7-8 at 165°C, and zones 9-11 at 160°C. The screw speed was set at 200 rpm. Pellets of polylactide (PLA) polymer, which is a copolymer of lactide with 0.35 wt. percent of epoxidized soybean oil and having a number average molecular weight of 104,000 and a D-level of 11%, available from Cargill, were fed into zone 1 at a rate of 123 g/min using an AccuRate feeder. A plasticizer, acetyl tri-n-butyl citrate from Morflex, Inc. was injected into zone 3 of the extruder at ambient temperatures using a liquid injection system. The plasticizer was fed in at a rate of 31.5 g/min providing a composition of 20.4% plasticizer.

The compounded mixture containing 20% plasticizer was then dry blended with sufficient amounts of the PLA used in the initial compounding (Mn-104,000, D-level of 11%) to obtain mixtures of 0, 5, 10, 15, and 20% plasticizer. These mixtures were then extruded on a

3/4" Killion extruder, through a six inch flat die, into film having a 3.25 mil thickness (0.00325"). The Killion extruder operated with zone 1 at 280°F, zone 2 at 290°F, zone 3 at 300°F, and zone 4, the adapter, and the die all at 315°F.

The glass transition temperature ( $T_g$ ) for each film was determined using Differential Scanning Calorimetry (DSC) according to procedure known in the art. A typical procedure includes taking a small sample of the film (5-20 mg) and placing it in a sealed capsule. The capsule is loaded in to the DSC and cooled to a temperature well below the expected  $T_g$ , e.g., -100°C. The sample is then heated at a rate between 5°C/min and 20°C/min and the heat input relative to a blank reference cell is recorded. The glass transition temperatures are evaluated, and recorded as the midpoint of the typical sigmoidal curve. The sample is evaluated on the first upheal of the DSC, to avoid any mixing of the sample phases.

The films were then aged and tested for tear propagation resistance and for blocking resistance. The tear propagation resistance test was conducted according to ASTM Method D 1922-89. The blocking resistance test involved placing two films on top of each other and placing thereon a 400 gm weight with a 2.2 in<sup>2</sup> contact area. This was left in a temperature controlled environment for 2.0 hours at 50°C and checked for blocking. The blocking scale for this test ranges from 0 for no blocking to 5 for complete fusion of the two layers. The results of the tear propagation resistance and blocking resistance tests are provided in Table 1.

Table 1

Percent Plasticizer	Elmendorf Tear (gm <sub>f</sub> )		Blocking Level	T <sub>g</sub> (°C)	Normalized Elmendorf (gm <sub>f</sub> /mil)	
	MD (avg)	TD (avg)			MD	TD
0	18	14	1	60	5.5	4.3
5	19.7	21.8	2	52	6.1	6.7
10	31.2	26.33	4	41	9.6	8.1
15	704	816	5	30	220	250
20	1,510	1600+	5	19	460	490

The results in Table 1 indicate that blocking resistance is inversely related to tear propagation resistance for single layer, plasticized films of polylactide. The results further indicate that the glass transition temperature (T<sub>g</sub>) is directly related to the amount of plasticizer therein. It is a discovery of the present invention that highly plasticized films of polylactide, while providing the desired properties of low T<sub>g</sub> and high tear strength, develop severe blocking problems. It should be appreciated that a blocking level of 1 indicates that there was substantially no blocking which indicates that there was at most minor adhesion but that the films could be pulled apart without significant deformation.

The normalized Elmendorf tear values are used to get approximate tear values of a 1 mil film.

Example 2Example Showing Multilayer Film with Good  
Blocking Resistance and Good Tear Propagation Resistance

5           A multilayer film was produced on a 10", four  
layer, Streamlined Coextrusion Die (SCD) blown film die  
manufactured by Brampton Engineering. Layer  
configuration of the die is as follows from outside to  
inside layers of the die, A/B/D/C. Three 3 1/2" David  
10 Standard extruders fed the A, D, and C layers while a 2  
1/2" David Standard extruder fed B layer. The process  
line also utilized a Brampton Engineering rotating air  
ring for polymer cooling. Layers B and D contained PLA  
(Mn = 103,000, D-level of 11%) plasticized with 20%  
15 Citroflex which was compounded as described in Example  
1. Layers A and C contained PLA (Mn = 66,000, D-level  
of 3%) dry blended with 10% Biopol D300G, supplied by  
Zeneca Corporation. Layer ratios for the film were A-  
19%, C=21%, combination of B and D = 60% of the total  
20 film structure. The thickness of the film produced was  
2.25 mil (0.00225"). The processing conditions for the  
film are provided in Table 2.

Table 2

	Extruder A	Extruder B	Extruder C	Extruder D
Zone 1	300	300	300	300
Zone 2	310	310	310	310
Zone 3	320	320	320	320
Zone 4	340	330	330	340
Zone 5		340	340	
Scn Chngr	330	330	330	330
Adapter 1	330	330	330	330
Adapter 2	330	330	330	330
Adapter 4	330	330	330	330
Die 1	330	330	330	330
Die 2	330	330	330	330
Die 3	330	330	330	330
Pressure	1,280	1,670	1,640	1,310
Melt Temp	336	338	338	339
Screw Spd	14	50	48	12
Amps	50	40	45	120
Line Spd	122 fpm			
Notes	PLA/Biopol blend	Plasticized PLA	Plasticized PLA	PLA/Biopol blend

**Note:** Temperatures in table 2 are given in °F.

Tear propagation resistance and blocking resistance testing was conducted on the multilayer film according to the procedure described in Example 1. The test results are provided in Table 3. Additionally, the multilayer film exhibited no sign of blocking when tested at 70°C for 24 hours.

**Table 3**

Elmendorf Tear (gm <sub>f</sub> )		Blocking Level	Normalized Elmendorf Tear (gm <sub>f</sub> /mil)	
MD (avg)	TD (avg)		MD	TD
112	242	0 @ 70°C	50	107

The results in Table 3 indicate that the non-plasticized outer layers prevent blocking while the plasticized inner layers provide the tear resistance of the film.

The normalized Elmendorf tear, although not recommended by ASTM, can be used to provide an estimate of the tear strength of a 1 mil film.

**Example 3:****Example showing Use of Non-PLA Materials in Multi-Layer Film Structures**

Films were produced on a 6" 7-layer SCD blown film die manufactured by Brampton Engineering, Inc. with a die gap of 0.060" and a Uni-Flo air ring for film cooling. Labeling of the die layers are from outside to inside A, B, C, D, E, F, G. Layers B, C, D, E, and F were fed by five 30 mm Brampton extruders. Layers A and G were fed by two 45 mm Brampton extruders. In making the film samples layers A and G were filled with 0.85MI (melt index) polyethylene and cooled down to 100°F to "freeze" the layers and effectively make the die a five-layer system. Structures were produced containing materials other than PLA as the base material for one or

more of the film layers. When plasticized PLA was utilized it was prepared in accordance to the method described in Example 1. Again only the B, C, D, E, and F layers of the die were utilized to produce the films.

5 In all of these films there was an attempt to make a flexible core layer surrounded by rigid, non-blocking outer layers.

**Table 4**

Sample	Material				
	Layer B	Layer C	Layer D	Layer E	Layer F
1	PLA	PVOH	PVOH	PVOH	PLA
2	PLA	Polyethylene	Polyethylene	Polyethylene	PLA
3	Biopol	Plasticized PLA	Plasticized PLA	Plasticized PLA	Biopol
4	EVOH	Plasticized PLA	Plasticized PLA	Plasticized PLA	EVOH

10

In all of the above cases except for sample #3 there was poor adhesion between the PLA layers and the "other" material layers. In the case of sample #3 a film with 5% layer ratios for B and F layers was

15 accomplished. This film showed no blocking at the haul off nip and also demonstrated a blocking level of 0 when tested in accordance to the test described in Example 1. The PVOH was supplied as VINEX 2144 by Air Products And Chemicals, Inc., the PE was a LLDPE (grade 2045)

20 supplied by Dow, and the EVOH was supplied by Eval Corporation.

**Example 4**

25

**Example Showing Effects of Layer Ratios on Physical Properties**

Films were processed on the equipment described in Example 3 to produce films with varying



layer ratios. The outer layers, layers B and F, utilized PLA dry blended with 10% Biopol D300G. The inner layers of the film, layers C, D, and E, utilized PLA compounded with 20% Citroflex plasticizer as described in Example 1. The following films were produced with thickness ranging from 1.5-1.75 mil (0.0015"-0.00175").

**Table 5**

Sample #	B Layer Ratio (%)	C,D,E, Combined Layer Ratio (%)	F Layer Ratio (%)
1	25	50	25
2	20	60	20
3	15	70	15
4	10	80	10
5	5	90	5

10

The films were conditioned in a 50% relative humidity chamber at 20-25°C and tested for tear propagation resistance according to ASTM D-1922, tensile properties according to ASTM D-882 method A3, and impact resistance according to ASTM D-3420 with the results provided in Table 6.

15



The data in Table 6 demonstrates the effect the layer ratios have on the tear propagation resistance, the yield strength, and the impact strength. Increasing the thickness of the inner, flexible layer, and decreasing the thickness of the outer layers, provides high tear resistance and impact strength, although yield is reduced. The data also demonstrates that the layer ratios do not have much of an effect on the ultimate tensile strength, the ultimate elongation, or the yield elongation.

The normalized tear force is provided as an estimate for a 1 mil film, although it is preferred to test a 1 mil film directly.

#### Example 5

#### Example Showing Compostable Properties of Coextruded Film

The multilayer film of Example 2 was tested to determine the rate and extent of degradation in a compost environment. For comparative purposes, sample of kraft paper and cellulose were similarly tested to evaluate the rate and extent of degradation in a compost environment. The kraft paper was from a typical grocery bag and the cellulose was microcrystalline cellulose from Avicel.

For all three samples, a modified version of ASTM D5338-92 test was performed according to ASTM D5338-92 except that a constant temperature of 58°C was provided in order to more conveniently approximate natural composting conditions. The amount of material biodegraded was calculated based upon measuring the amount of carbon dioxide evolved therefrom.

Test results were plotted in the graph of FIG.3 as "Cumulative % Biodegradation (CO<sub>2</sub>-C)" as a function of time. The graph demonstrates that the multilayer film of Example 2 degrades at a rate and to an extent fairly close to cellulose and kraft paper.

Comparative Example 1

Monolayer films having a thickness of 2 mil were prepared from polybutylene(succinate) and from polybutylene(succinate-adipate copolymer). The polymer samples are available as Bionolle® 1001 and 3001 from Showa Highpolymer Co., Ltd. The films were blown using a 1" Killion die and 1" Killion single screw general purpose extruder with 3:1 compression ratio and 24:1 L:D. A single tip air ring was used to provide bubble inflation. Throughput was about 8 lb/hr.

The films were tested for Elmendorf tear following ASTM D1922-89, with the following results, all in grams-force (gm<sub>f</sub>).

15

polybutylene(succinate)			polybutylene(succinate-adipate copolymer)	
Temperature	MD	TD	MD	TD
23°C	31	49	34	54
10°C	26	35	29	43
0°C	31	34	30	44

The polybutylene(succinate) film exhibited a Tg of -37°C and 47.4 J/g crystallinity, with a peak melting point of 113°C. The polybutylene(succinate-adipate copolymer) film had a Tg of -45°C and 34 J/g crystallinity, with a melting temperature of 94°C. The strength, however, is insufficient for commercial use as a lawn refuse bag.

25

Example 6

Two films were prepared on a multilayer blown film line to prepare a A-B-A composition. The "A" material was fed using a 3/4" Brabender general purpose extruder, the "B" material was fed using a 1" Killion general purpose extruder, and the die was a 1" Killion 3-layer die side fed, with a 0.030" die gap. The "A"

30

material was fed at a rate of 3.6 lb/hr and had a melt temperature of 365°F. The "B" material was fed at 8.4 lb/hr and had a melt temperature of 325°F. A single lip air ring was used for inflation and the film take-off speed was about 10-30 ft/min.

The core layer in each case consisted of poly(lactide) with a number average molecular weight of about 100,000 and which included 0.35 wt% of epoxidized soybean oil in the polymerization. The overall optical composition was 85% S-lactic acid residuals and 15% R-lactic acid residuals, from lactide. The core layer additionally contained 20 wt% of the plasticizer acetyl ti-n-butyl citrate, available as Citroflex™ A-4 from Morflex, Inc. The outer layer for film one was a blend of 90 wt% poly(lactide) and 10 wt% poly(hydroxy butyrate-co-hydroxy valerate), called PHBV for short, available as Biopol™ D300G from ICI.

For the first multilayer film, the outer layer included a polylactide polymer containing 0.35 wt% epoxidized soybean oil added prior to polymerization in a batch reactor and having a number average molecular weight of about 90,000 and an overall optical composition including 95% S-lactic acid residuals and 5% R-lactic acid residuals.

For the second multilayer film, the outer layer included a polybutylene(succinate) polymer, available as Bionolle 1001 from Showa Highpolymer Co., Ltd.

**THIS PAGE BLANK (USPTO)**

**THIS PAGE BLANK (USPTO)**

Both multilayer films were 2 mil thick and had a layer ratio of 15/70/15 percent by weight. Table 7 shows the Elmendorf tear results in gm<sub>f</sub>, according to ASTM D1922-89, for each multilayer film wherein the films are identified by their outer layer.

Table 7

poly(lactide)/PHBV blend outer layer			polybutylene(succinate) outer layer [3054-8-2]	
Temperature	MD	TD	MD	TD
23°C	93	150	172	176
10°C			80	79
0°C	12	17	47	54

The tests show that each film exhibits good tear strength at 23°C. The low temperature tear strength of the film with an outer layer of polybutylene(succinate) was superior to the film with an outer layer of poly(lactide)/PHBV. It is believed that the low T<sub>g</sub> (estimated to be less than -30°C) of the outer layer for film two assists in giving good properties at low temperature.

Example 7

Two films, each 2 mil thick, were prepared on a blown film line according to the procedure described in Example 10. Each film included a core layer of polylactide with 85-88% S-lactic acid residuals and 12-15% R-lactic acid residuals (from lactide) to form an amorphous film with number average molecular weight of 85,500 for film 1 and 106,000 for film 2. The polylactide included 0.35 wt% of epoxidized soybean oil included during the polymerization, carried out in a batch reactor. The polymer was blended with 25 wt% of a plasticizer which was tri-n-butyl citrate, available as Citroflex™ C-4 from Morflex, Inc. The Elmendorf tear properties are shown in the table 8.



Table 8

polybutylene(succinate ) outer layer (film 1)			polybutylene(succinate) outer layer (film 2)	
Temperature	MD	TD	MD	TD
23°C	186	304	139	147
10°C			72	110
0°C	47	66	76	75

5 Film 1 exhibited two Tg's, one at about -35°C  
corresponding to the outer layer and one at 8.6°C for  
the plasticized poly(lactide) core layer. The outer  
layer exhibited a Tm of 109°C with 16.7 J/g on a whole  
film basis, corresponding to 56 J/g on an outer layer  
basis. DSC results are not available on film 2.

10 Each of these two samples shows good tear  
strength and had good blocking resistance to at least  
60°C.

## WHAT IS CLAIMED:

1. A compostable multilayer film comprising:
  - (a) core layer comprising a lactic acid residue containing polymer having a  $T_g$  below about 20°C, and  
5 having first and second opposed surfaces;
  - (b) first blocking reducing layer covering the first surface of said core layer, said first blocking reducing layer comprising a semicrystalline polymer composition; and  
10 (c) second blocking reducing layer covering the second surface of said core layer;  
wherein at lease one of said blocking reducing layer comprises a semicrystalline polymer composition.
- 15 2. The compostable multilayer film according to claim 1, wherein said lactic acid residue containing polymer comprising a polylactide polymer has a crystallinity of greater than 10 J/g as determined by a differential  
20 scanning calorimeter.
3. The compostable multilayer film according to claim 1, wherein the blocking reducing layer comprising a semicrystalline polymer composition has a crystallinity of greater than 30 J/g as determined by a differential  
25 scanning calorimeter.
4. The compostable multilayer film according to claim 1, wherein said semicrystalline polymer composition comprises an aliphatic polyester.  
30
5. The compostable multilayer film according to claim 4, wherein the aliphatic polyester comprises a polymer selected from the group consisting of  
35 polyethylene(oxalate), polyethylene(succinate), polybutylene(oxalate), polybutylene(succinate), polypentamethyl(succinate), polyhexamethyl(succinate), polyheptamethyl(succinate), polyoctamethyl(succinate), polyethylene(succinate-co-adipate),

polybutylene(succinate-co-adipate),  
polybutylene(oxylate-co-succinate),  
polybutylene(oxylate-co-adipate), and mixtures thereof.

5 6. The compostable multilayer film according to claim  
1, wherein the semicrystalline polymer comprises  
polybutylene succinate homopolymer.

10 7. The compostable multilayer structure according to  
claim 1, wherein said compostable multilayer film has a  
biodegradability value of about 20 percent or higher  
after 40 days according to ASTM D5338-92, modified to  
test at about 58°C.

15 8. The compostable multilayer structure according to  
claim 1, wherein said compostable multilayer structure  
has a biodegradability value of about 50 percent or  
higher after 40 days according to ASTM D5338-92,  
modified to test at about 58°C.

20 9. The compostable multilayer structure according to  
claim 1, wherein the polylactide polymer is a copolymer  
prepared by reacting lactide monomer and non-lactide  
acid monomer.

25 10. The compostable multilayer structure according to  
claim 9, wherein non-lactide monomer is epoxidized  
multifunctional oil.

30 11. The compostable multilayer structure according to  
claim 1, wherein at least one of the blocking reducing  
layers includes an antiblocking polymer additive  
selected from the group consisting of  
poly(hydroxybutyrate) and poly(hydroxybutyrate-co-  
35 hydroxyvalerate).

12. The compostable multilayer structure according to claim 1, wherein the core layer is peroxide modified to reduce plasticizer migration.
- 5 13. A method for manufacturing a compostable multilayer film, said method comprising the step of: coextruding at least three layers, said layers comprising
- (a) core layer comprising a lactic acid residue containing polymer having a  $T_g$  below about 20°C, and
  - 10 having first and second opposed surfaces;
  - (b) first blocking reducing layer covering the first surface of said core layer; and
  - (c) second blocking reducing layer covering the second surface of said core layer; wherein at least one
  - 15 of said blocking reducing layers comprises a semicrystalline polymer composition.
14. The method for manufacturing a compostable multilayer film according to claim 13, further
- 20 comprising a step of blowing the layers.
15. The method for manufacturing a multilayer film according to claim 14, wherein the step of blowing comprises double bubble blowing.
- 25 16. The method for manufacturing a multilayer film according to claim 13, further comprising the step of blow molding.
- 30 17. A compostable multilayer film comprising
- (a) core layer comprising a lactic acid residue containing polymer and at least 20 percent by weight, based on the weight of the core layer, of a plasticizer, said core layer having first and second opposed
  - 35 surfaces;
  - (b) first blocking reducing layer covering the first surface of said core layer; and

(c) second blocking reducing layer covering the second surface of said core layer.

18. The compostable multilayer film according to claim 5 17, wherein at least one of the blocking reducing layers comprises a semicrystalline polymer composition having a crystallinity of greater than 10 J/g as determined by a differential scanning calorimeter.

10 19. The compostable multilayer film according to claim 17 wherein at least one of the blocking reducing layers comprises a polymer selected from the group consisting of polyethylene(oxalate), polyethylene(succinate), polyethylene(oxalate), polybutylene(succinate), 15 polypentamethyl(succinate), polyhexamethyl(succinate), polyheptamethyl(succinate), polyoctamethyl(succinate), polyethylene(succinate-co-adipate), polybutylene(succinate-co-adipate), polybutylene(oxylate-co-succinate), 20 polybutylene(oxylate-co-adipate), and mixtures thereof.

20. A compostable multilayer structure comprising:  
(a) compostable substrate;  
(b) core layer comprising a lactic acid residue 25 containing polymer composition covering said compostable substrate, said core layer having a  $T_g$  below about 20°C; and  
(c) blocking reducing layer covering said core layer.

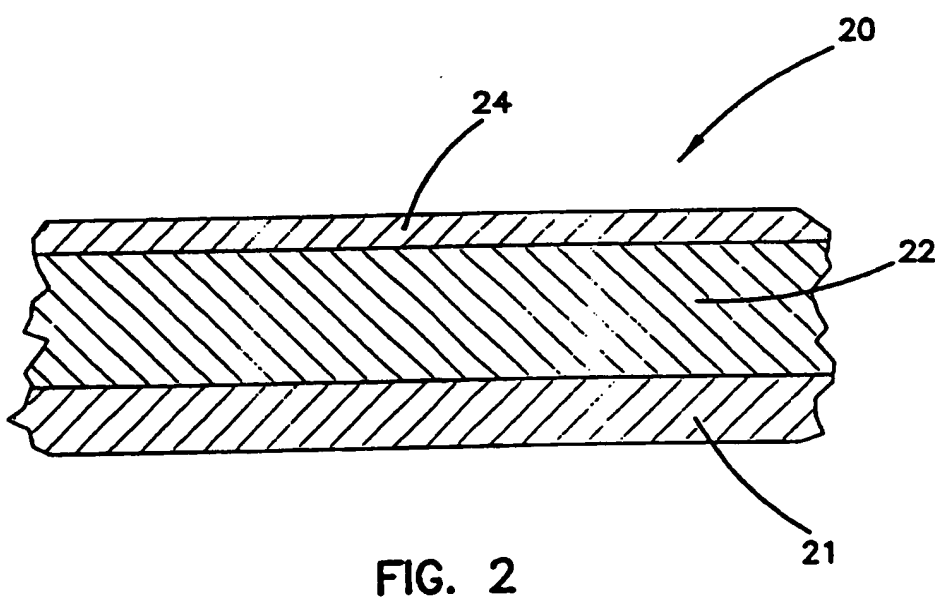
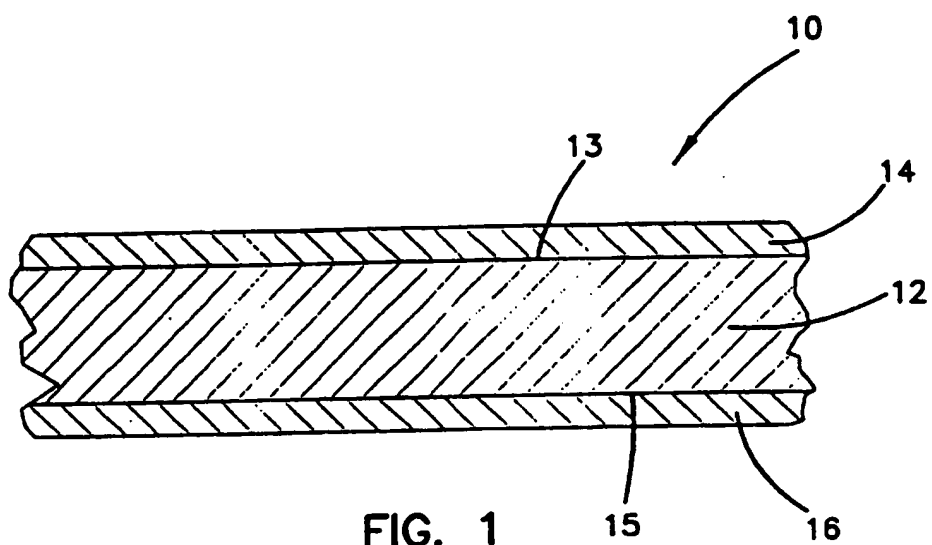
30

21. The compostable multilayer structure according to claim 20, wherein said compostable substrate comprises a cellulose containing substrate.

35 22. The compostable multilayer structure according to claim 20, wherein the cellulose containing substrate is paper.

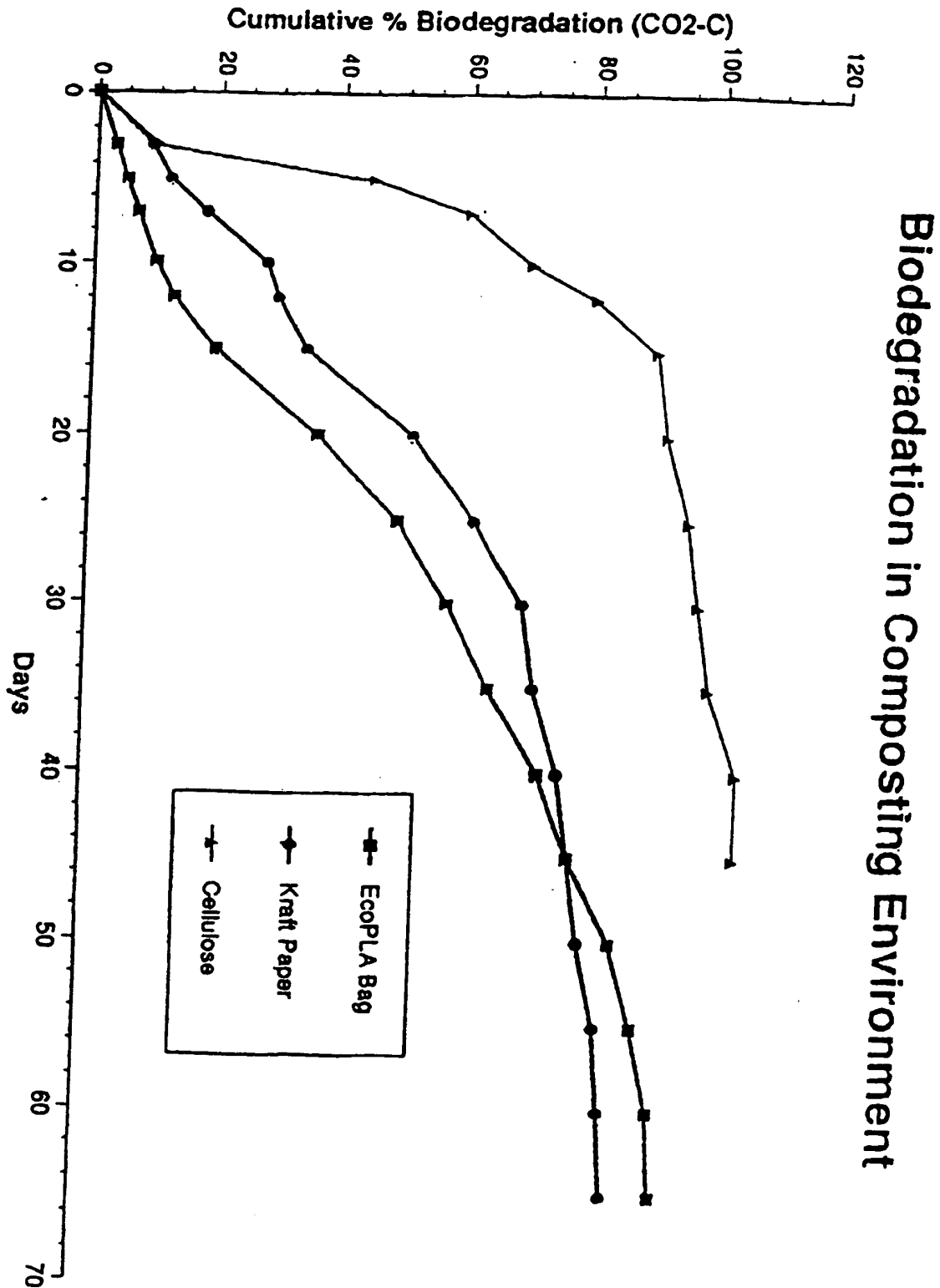
23. The compostable multilayer structure according to claim 20, wherein said core layer comprises a polylactide polymer and an effective amount of a plasticizer to provide a  $T_g$  for the core layer of below about 20°C.
24. A compostable film comprising a lactic acid residue containing polymer, said film having a tear resistance greater than 50 gm<sub>f</sub>/mil at 23°C according to ASTM D1922-89, and exhibiting substantially no blocking when folded back on itself and held together under a pressure of 180 g/in<sup>2</sup> at 50°C for two hours.
25. The compostable film according to claim 24, said film having a tear resistance greater than 65 gm<sub>f</sub>/mil at 23°C according to ASTM D1922-89.
26. The compostable film according to claim 24, said film having a tear resistance greater than 80 gm<sub>f</sub>/mil at 23°C according to ASTM D1922-89.
27. The compostable film according to claim 24, wherein said film exhibits substantially no blocking when folded back on itself and held together under a pressure of 180 g/in<sup>2</sup> at 50°C for twenty four hours.
28. The compostable film according to claim 24, wherein said film comprises a multilayer film.

1/2



2/2

FIG 3





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15682**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : 428/35.7, 480, 481; 528/272, 354, 361, 365, 366

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/35.7, 480, 481; 528/272, 354, 361, 365, 366

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: polylactide, lactic acid, polyester, laminate, Tg. blocking, biodegradable.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,444,113 A (SINCLAIR ET AL) 22 August 1995 (22.08.95), column 8, lines 33-53; column 16, lines 40-53; column 25, line 65 to column 26, line 6; column 27; column 29, lines 24-49; column 33, lines 1-8; columns 36-37.	1-3, 7-9, 13-18, 20-28
Y	US 5,108,807 A (TUCKER) 28 April 1992 (28.04.92), column 4, lines 55-65; column 6, lines 30-63; column 7, lines 3-7, 27; column 10, lines 3-19; column 12, lines 35-50; column 13, lines 23-43.	4-6, 19
Y	US 5,359,026 A (GRUBER) 25 October 1994 (25.10.94), column 3, line 50 to column 4, line 23; Table 2.	9-10

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

25 NOVEMBER 1996

Date of mailing of the international search report

17 JAN 1997

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PAUL THIBODEAU

Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

Int. national application No.  
PCT/US96/15682

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,180,765 A (SINCLAIR) 19 January 1993 (19.01.93), column 15, lines 50-59.	12

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/15682

## A. CLASSIFICATION OF SUBJECT MATTER: IPC (6):

B32B 27/08, 27/10, 27/36; C08G 59/02, 63/02, 63/06, 63/08, 63/12, 63/16, 63/02

**THIS PAGE BLANK (USPTO)**